COATINGS ON FIBER REINFORCED COMPOSITES

FIELD OF THE INVENTION

This invention relates to thermal spray coatings for fiber reinforced polymeric composites. This invention also relates to a process for producing the coatings and to articles of manufacture having fiber reinforced polymeric composite components with the coatings.

BACKGROUND OF THE INVENTION

Fiber reinforced composite materials with polymeric matrices (FRP) including carbon fiber reinforced polymers (CFRP) can be designed and constructed that have outstanding mechanical and physical properties such as low density, high tensile and torsional strength, and high modulus of elasticity or stiffness. A variety of high strength fiber materials can be used including carbon fibers, glass fibers, silicon carbide fibers, and fibers of many other oxides, carbides, and other materials. Similarly, a wide variety of polymeric materials can be used including thermosetting resins such as phenolic resins, epoxies, and many others. The fibers may be very long and positioned in specific patterns or relatively short and randomly dispersed. When long

fibers are positioned in specific patterns, they can be aligned in a single direction or positioned in patterns designed to give two or three dimensional strength to the FRP. Thus the mechanical properties of the FRP

5   structure can be tailored to the specific requirements of a component.

Unfortunately, the surfaces of a FRP have low resistance to wear including adhesive, abrasive, and erosive wear. They may also be susceptible to

10 oxidation or other forms of corrosion, need protection from heat, not have the required optical or electrical characteristics, etc. As a result, their utilization has been limited in many applications or has required the use of metallic or ceramic inserts or sleeves in

15 areas of contact or exposure to wear, heat, etc. For example, a bulky and expensive wear resistant sleeve must be bonded to a FRP shaft in bearing areas to prevent adhesive or abrasive wear and FRP aircraft wing or tail components must have a metallic shield bonded

20 on leading edges to prevent erosion. If the large rolls used in paper manufacturing and printing industries could be made of FRP they would be much lighter and stiffer thus much easier and safer to handle, require less energy and time to accelerate and

25 decelerate (due to lower inertia), and produce better products due to rigidity. Their surface, however, would not have adequate wear resistance and could not be engraved as is required for some printing applications.

30 A solution to many of the problems associated with the utilization of FRP would be an adherent coating with the required wear resistance or other properties.

A wide variety of metallic, ceramic, cermet, and some polymeric coatings can be produced using thermal spray deposition. Many of these materials would be useful in providing wear resistance and other properties for FRP

5   components if they could be successfully deposited on them.

The family of thermal spray processes includes Super D-Gun™ deposition, detonation gun deposition, high velocity oxy-fuel deposition and its variants such

10   as high velocity air-fuel, plasma spray, flame spray, and electric wire arc spray. In most thermal coating processes, a metallic, ceramic, cermet, or some polymeric material in powder, wire, or rod form is heated to near or somewhat above its melting point and

15   droplets of the material accelerated in a gas stream. The droplets are directed against the surface of the substrate (part or component) to be coated where they adhere and flow into thin lamellar particles called splats. The coating is built up of multiple splats

20   overlapping and interlocking. These processes and the coatings they produce have been described in detail in the following: "Advanced Thermal Spray Deposition Techniques", R. C. Tucker, Jr., in <u>Handbook of Deposition Technologies for Films and Coatings</u>, R. F.

25   Bunshah, ed., Second Edition, Noyes Publications, Park Ridge, New Jersey, 1994, pp. 591 to 642; "Thermal Spray Coatings", R. C. Tucker, Jr. in <u>Handbook of Thin Films Process Technology</u>, Institute of Physics Publishing, Ltd., London, 1995; and "Thermal Spray Coatings", R. C.

30   Tucker, Jr., in <u>Surface Engineering, ASM Handbook</u>, Vol.

5, ASM International, Materials Park, Ohio, 1994, pp. 497-509.

In virtually all thermal spray processes, two of the most important parameters controlling the structure
5 and properties of the coating are the temperature and the velocity of the individual particles as they impact on the surface to be coated. Of these, the temperature of the particles is of greatest import relative to coating FRPs. The temperature the particles achieve
10 during the deposition process is a function of a number of parameters including the temperature and enthalpy (heat content) of the process gases, the specific mechanisms of heat transfer to the particles, the composition and thermal properties of the particles,
15 the size and shape distributions of the particles, the mass flow rate of the particles relative to the gas flow rate, and the time of transit of the particles. The velocity the particles achieve is a function of a number of parameters as well, and some of these are the
20 same as those that affect the particle temperature including the composition, velocity and flow rate of the gases, the size and shape distributions of the particles, the mass injection rate and density of the particles.
25 In a typical detonation gun deposition process, a mixture of oxygen and acetylene along with a pulse of powder of the coating material is injected into a barrel about 25 mm in diameter and over a meter long. The gas mixture is detonated, and the detonation wave
30 moving down the barrel heats the powder to near or somewhat above its melting point and accelerates it to velocity of about 750 m/s. The powder's rapidly heated

into molten, or nearly molten droplets of material that strike the surface of the substrate to be coated and flow into strongly bonded splats. After each detonation the barrel is purged with an inert gas such

5   as nitrogen, and the process repeated many times a second. Detonation gun coatings typically have a porosity of less than two volume percent with very high cohesive strength as well as very high bond strength to the substrate. In the Super D-Gun™ coating process,

10   the gas mixture includes other fuel gases in addition to acetylene. As a result there is an increase in the volume of the detonation gas products which increases the pressure and hence greatly increases the gas velocity. This, in turn, increases the coating

15   material particle velocity, which may exceed 1000 m/s. The increased particle velocity results in an increase in coating bond strength, density, and an increase in coating compressive residual stress. In both the detonation gun and Super D-Gun coating processes

20   nitrogen or another inert gas can be added to the detonation gas mixture to control the temperature of the detonated gas mixture and hence the powder temperature. The total process is complex, and a number of parameters can be used to control both the

25   particle temperature and velocity, including the composition and flow rates of the gases into the gun.
          In high velocity oxy-fuel and related coating processes oxygen, air, or another source of oxygen is used to burn a fuel such as hydrogen, propane,

30   propylene, acetylene, or kerosene in a combustion chamber and the gaseous combustion products allowed to expand through a nozzle. The gas velocity may be

supersonic. Powdered coating material is injected into the nozzle and heated to near or above its melting point and accelerated to a relatively high velocity, up to about 600 m/s for some coating systems. The

5   temperature and velocity of the gas stream through the nozzle, and ultimately the powder particles, can be controlled by varying the composition and flow rate of the gases or liquids into the gun. The molten particles impinge on the surface to be coated and flow into

10   fairly densely packed splats that are well bonded to the substrate and each other.

In the plasma spray coating process a gas is partially ionized by an electric arc as it flows around a tungsten cathode and through a relatively short

15   converging then diverging nozzle. The partially ionized gas, or gas plasma, is usually based on argon, but may contain, for example, hydrogen, nitrogen, or helium. The temperature of the plasma at its core may exceed 30,000 K and the velocity of the gas may be

20   supersonic. Coating material, usually in the form of powder, is injected into the gas plasma and is heated to near or above its melting point and accelerated to a velocity that may reach about 600 m/s. The rate of heat transfer to the coating material and the ultimate

25   temperature of the coating material are a function of the flow rate and composition of the gas plasma as well as the torch design and powder injection technique. The molten particles are projected against the surface to be coated forming adherent splats.

30   In the flame spray coating process, oxygen and a fuel such as acetylene are combusted in a torch. Powder, wire, or rod is injected into the flame where

it is melted and accelerated. Particle velocities may reach about 300 m/s. The maximum temperature of the gas and ultimately the coating material is a function of the flow rate and composition of the gases used and
5 the torch design. Again, the molten particles are projected against the surface to be coated forming adherent splats.

Many attempts have been made to directly coat FRP surfaces with thermal spray coatings. Thermal spray
10 coatings of metallic, cermet, or ceramic compositions usually do not adhere at all or spall when only a small amount of coating has been deposited. In most thermal spray coating applications, the surface to be coated must be roughened to provide adequate bonding.
15 Roughening is usually done by grit blasting the surface. Grit blasting or some other forms of roughening FRP surfaces leads to unacceptable erosion of the polymeric matrix and fraying of the fibers. The later, in particular, leads to a rough and porous
20 thermal spray coating. This and other problems were found in attempting the method of Hycner in U.S. Patent 5,857,950 for example. Hycner teaches grit blasting the surface of a CFRP fluid metering roll (an anilox roll used in printing) and then thermal spraying a
25 layer of zinc, nickel-20 chromium, or mixture of aluminum bronze plus 10 polyester at a negative rake angle of 11 ½ to 13 ½ degrees. A ceramic coating is then applied over the first layer. The ceramic coating is subsequently finished and engraved. This process
30 has been found to be unacceptable because of poor bond strength with some of the specified first layer coatings and other production problems and because of

substantial imperfections in the coating. Many other
attempts to use thermally sprayed metallic undercoats
have also failed. Even attempts to deposit an
undercoat of a polymeric material by thermal spraying
5   were only marginally successful in laboratory
experiments and in production were difficult to
reproduce in a reliable manner.

An alternative method has been taught by Habenicht
in EP 0 514 640 B1. Habenicht first creates on the
10   surface of a CFRP a layer that consists of a mixture of
a synthetic resin that bonds to the CFRP and a
particulate material. After this layer is cured the
surface is partially removed to expose the particulate
material. The particulate material must be capable of
15   chemical bonding to the outer coating material that is
thermally sprayed on the first layer. The particulate
materials and the outer thermal spray coating material
are selected from variety of metals and ceramics.
While this method has met with limited success, the
20   mixture of synthetic resin and particulate material may
not bond well to the CFRP and tends to form balls of
material on the surface, thus being unsuitable for
commercial production.

Several other techniques of preparing the surface
25   of a CFRP surface for thermal spray coatings have been
described by E. Lugscheider, R. Mathesius, G. Spur, and
A. Kranz in the Proceedings of the 1993 National
Thermal Spray Conference, Anaheim, California, 7 to 11
June 1993. One method appears to be similar to that of
30   Habenicht, but the most successful method appeared to
be one in which a three dimensional wire mat was
laminated into the polymeric composite. The surface

was then grit blasted to expose the wire and a thermal spray coating applied. This technique would be very expensive to use in industrial applications and would tend to yield a very rough surface on the thermal spray
5   coating.

Thus the current state of the art is such that there appears to be no method of successfully depositing thermal spray materials of a wide variety of compositions on FRP in a production worthy manner.

10   It is an object of the present invention to provide a coating for fiber reinforced composite polymeric materials and components that are well bonded and have an exterior layer with high resistance to wear, corrosion or other unique properties not provided
15   by the fiber reinforced composite materials.

It is further object of the present invention to provide a process for applying well bonded thermal spray coatings to fiber reinforced composite polymeric materials.

20   It is a particular object of the invention is to provide a thermal spray coating and a method of applying thermal spray coating to carbon fiber reinforced composite materials and components.

25   SUMMARY OF THE INVENTION

The invention is a coating for fiber reinforced composite materials. A first polymeric layer, free of fibers and particulate, coats a fiber reinforced polymer substrate. The first layer joins the fiber
30   reinforced polymer substrate to a second polymeric layer—two different composites. The second polymeric layer contains a polymeric matrix and a particulate

within the polymeric matrix. Finally, at least one thermally sprayed material coats the second polymeric layer to form an adherent multi-layer coating attached to the fiber reinforced polymer substrate.

5   The process of the invention applies a coating on a fiber reinforced composite material. It includes the steps of applying a first polymeric layer to a fiber reinforced polymer substrate. The first polymeric layer is free of fibers and particulate. Applying a

10   second polymeric layer coats the first polymeric layer. The first polymeric layer acts as a bonding agent to join the fiber reinforced polymer substrate to the second polymeric layer. The second polymeric layer contains a polymeric matrix and a particulate within

15   the polymeric matrix. Thermal spraying a material coats the second polymeric layer, with the first and second polymeric layers protecting the fiber reinforced polymer substrate during thermal spraying.

20   DESCRIPTION OF THE PREFERRED EMBODIMENTS

As noted above, it has been found that adequate thermal spray coatings on fiber reinforced composite materials can not be achieved using known methods. Surprisingly, it has been found that by applying a

25   first layer comprising only polymeric materials and then a second layer comprising a mixture of polymeric and particulate materials, that one or more additional layers of thermal spray materials can be applied. It is necessary to judicially choose the polymeric

30   materials in the two initial layers to achieve high bond strength between the first layer and the FRP and between the first and second layer. With an

appropriate choice of materials, very well bonded
coatings with no significant imperfections can be
deposited.

The polymeric materials that may be used in either
5   the polymeric first layer or as the polymeric material
in the second layer comprising a mixture of polymeric
and particulate materials include epoxies and
thermosetting resins. The preferred polymeric
materials are epoxies and the most preferred polymeric
10 material is bisphenol F/epichlorohydrin epoxy resin
(Shell Epon Resin 862) mean hydrogen equivalent weight
of curing agent / epoxy equivalent weight of resin =
20.7 / 170 = .1218 or 12.18 weight percent of curing
agent diethylenetriamine (Epi-Cure 3223), a two part
15 epoxy that cures at room temperature. The first
polymeric layer remains free of fibers and particulate
to ensure a strong bond to the FRP.

The surface of the FRP must be cleaned prior to
the application of the first layer. Appropriate
20 solvents may be used to remove any oils or other
contaminants. It is preferred that the surface be
roughened after it has been cleaned, preferably to a
roughness of not less than 3.048 microns (120
microinches) Ra. Grit blasting can be used to
25 accomplish the surface roughening. Residual debris and
other contaminants can be removed by wiping with an
appropriate solvent such as methanol or acetone.

A variety of methods may be used to apply the
first layer of polymeric materials. The choice of
30 method is dependent, in part, on the geometry of the
surface to be coated and the composition and physical
characteristics of the polymeric material. The methods

include spreading the polymeric material on surface if it is sufficiently viscous, spraying atomized droplets of the materials using typical liquid spray dispensers or any other method of applying a liquid to a surface.

5   Spreading a viscous material on the surface may be done manually or with an automated or semi-automated system. A doctor blade may be used to control the thickness of the layer. The polymeric material may be applied by spraying, if the viscosity is low enough or a diluent

10   is added to the polymeric material to reduce its viscosity sufficiently to allow spraying. The preferred method is to spread the polymeric material on the surface as somewhat viscous material, most preferably using an automated or semi-automated method.

15   If the surface to be coated is cylindrical in shape, the cylinder can be rotated and the polymeric material applied to the surface by feeding it onto a blade held parallel to an element of the cylinder surface and at a distance suitable to control the thickness of the

20   layer. The polymeric material is then allowed to flow off of the blade surface onto the cylinder surface as a smooth sheet of uniform thickness. The thickness is thus controlled and no mist or overspray is released into the atmosphere as is the case in spraying.

25   Preferably only a thin layer of the polymeric material is applied to the surface of the FRP, just sufficient to wet the surface. The preferred thickness of the layer comprising a polymeric layer is in the range of about 0.002 to 0.127 mm, with the most preferred range

30   being about 0.005 to 0.076 mm.

    The second layer of the coating system comprising a mixture of polymeric and particulate materials is

usually applied over the first layer comprising a
polymeric material before the first layer is cured;
i.e., while the first layer is still tacky.
Alternatively, the first layer comprising a polymeric
5   material is cured after it is applied. If necessary,
and a thick enough layer is applied, the cured first
layer may be machined by grinding or other methods to
smooth and adjust the thickness of the layer.

The particulate material in the second layer may
10   be at least one material selected from the group
consisting of metallics, cermets, and ceramics. Most
advantageously, the particulate is at least one
material selected of the groups consisting of: Group I,
aluminum, nickel, iron, chromium, and cobalt; Group II,
15   aluminum-base, nickel-base, iron-base, chromium-base,
and cobalt-base alloys; Group III, aluminum, chromium,
zirconium and silicon oxides; Group IV, aluminum,
chromium, zirconium and silicon compounds; Group V,
chromium, tungsten, boron, silicon carbides; and Group
20   VI, boron and chromium nitrides. The size of the
particulate material is dependent on the specific
composition of the particulate material, but may be
from essentially zero to about 500 µm (less than
approximately 50 mesh). The preferred size for greater
25   than 90% of the material for aluminum is -127/+78 µm
screen size (-200/+325 mesh), for nickel is -149/+78 µm
screen size (-170/+325 mesh), and for iron -318/+78 µm
screen size (-80/+325 mesh). For other particulate
materials, the preferred size is -318/+64 µm screen
30   size (-80/+400 mesh). The amount of particulate
material in the second layer is a function of the
composition of the particulate material, the geometry

of the component being coated, and the method of
application as small changes in composition can change
the viscosity of the mixture significantly. In weight
percent, the preferred amount of particulate material

5   is in the range of about 20 to 85, and the most
preferred amount is in the range of about 60 to 80.

The second layer of the coating system comprising
a mixture of a polymeric material and a particulate
material may be applied by any of the methods described

10   above for the first layer comprising a polymeric
material. The method used for the first layer may be
different than that used for the first layer, however,
depending on the physical characteristics of the
mixture. For example, the first layer may be sprayed

15   and the second spread. Nonetheless, the preferred
method for applying the second layer is by spreading
manually or in an automated or semi-automated manner.
If the surface to be coated is cylindrical in shape,
the most preferred method is by feeding the mixture

20   onto a blade held parallel to an element of the
cylinder and at a distance suitable to control the
thickness of the layer. The mixture is then allowed to
flow off of the blade onto the cylinder surface as a
smooth sheet of uniform thickness. The preferred

25   thickness of the layer comprising a mixture of
polymeric and particulate materials is in the range of
about 0.05 to 3.2 mm, with the most preferred range
being about 0.5 to 1.27 mm.

The second layer comprising a mixture of polymeric

30   and particulate materials is cured after it is applied.
If necessary, the cured second layer may be machined by
grinding or other methods to smooth the surface and to

adjust the thickness of the layer. The roughness of
the surface of the second layer may then be optimized
to increase the strength of the bond of the
subsequently applied thermal spray coating to it. The

5   preferred method of surface roughening is grit
blasting. Preferably, grit blast parameters are chosen
to obtain the maximum roughness without removing more
than about a 0.025 mm thick layer of material from the
surface.

10   One or more layers of thermal spray coatings are
applied by any thermal spray method over the suitably
prepared layer comprising a mixture of polymeric and
particulate material. Although any thermal spray
method may be used, the preferred method is plasma

15   spray deposition. Metallic, ceramic, cermet, and some
polymeric materials may be deposited by thermal spray.
As noted above, the specific thermal spray coating
material is selected based on the requirements of the
service environment. Enhanced mechanical properties

20   may be achieved by using two or more layers of thermal
spray coatings of different compositions. For example,
the first or inner thermal spray layer may be a metal
or metal alloy such as nickel or a nickel-chromium
alloy and the second or outer layer an oxide such as

25   chromium oxide. Such a two layer thermal spray coating
system may have a higher bond strength and greater
resistance to impact damage than a single layer of
chromium oxide. The thickness of the thermal spray
coating layer or layers is dependent on the

30   requirements of the service environment including the
expected wear life and mechanical properties. The
preferred thermal spray coating thickness range is

about 0.05 to 0.5 mm. The preferred thickness range is
about 0.05 to 0.25 mm for the initial metallic thermal
spray coating when two or more thermal spray coating
layers are used.

5   This invention is applicable to the coating of
many articles manufactured using fiber reinforced
composites to enhance the wear, corrosion, and other
properties of their surfaces. Virtually any component
geometry that can be coated using thermal spray
10   technology (a line-of-sight deposition process) can be
coated using the methods of this invention. Some of
the most readily coated component surfaces are those
that are either flat or cylindrical in shape.
Cylinders are usually coated by rotating them about
15   their axis and simultaneously applying the coatings by
moving the spreading or spraying application along the
length of the cylinder. Both the rate of rotation and
the rate of traverse down the length of the cylinder
are chosen to uniformly apply the coatings at a
20   prescribed rate of deposition in one or more passes.

          FRP cylinders of particular importance are rolls
used in the printing and in the paper industry as noted
in the background section herein. In the printing
industry, anilox rolls are used to transport very
25   precisely measured amounts of ink from a reservoir to
the printing roll. Currently, the most advanced rolls
of this type are made of metal with a plasma sprayed
chromium oxide surface. The chromium oxide is first
ground to a smooth surface and then engraved using a
30   laser with very small holes. Ink is adsorbed on the
surface as the roll rotates through a reservoir. The
excess ink is scrapped from the surface by a doctor

blade and then the remaining ink contained in the holes
is transferred to the printing roll. The roll surface
must be both resistant to corrosion by the ink and
resist wear by the doctor blade. An ideal material for
5   this application is chromium oxide. For the reasons
noted in the background section, it would be highly
advantageous to change from a metallic roll body to a
carbon fiber reinforced polymeric composite roll body.
After repeated unsuccessful trials using the various
10   methods known in the art, it was found that the methods
of this invention yielded a uniquely reproducible and
production worthy coating system for this application.

   The preferred coating system for anilox rolls
consists of a first layer comprising an epoxy-based
15   polymeric coating about 0.005 to 0.076 mm thick, a
second layer comprising a mixture of an epoxy-based
polymeric coating and a particulate material about 0.5
to 1.27 mm thick, a thermal spray coating layer of a
metal or metal alloy about 0.05 to 0.25 mm thick, and a
20   thermal spray coating of chromium oxide about 0.01 to
0.5 mm thick. The most preferred epoxy based polymeric
material in both the first and second layer is
bisphenol F/epichlorohydrin epoxy resin + 12.18 weight
percent diethylenetriamine. The preferred particulate
25   material in the mixture of the second layer mixture is
selected from the group consisting of metals, ceramics,
and cermets. The most preferred particulate material
in the mixture of the second layer is selected from the
group comprising aluminum, aluminum alloys, nickel,
30   nickel alloys, or iron alloys. The preferred amount of
particulate material in weight percent in the mixture
of polymeric and particulate materials in the second

layer is about 20 to 85. The most preferred amount of particulate material in weight percent in the mixture of the second layer is about 58 to 64 for aluminum and about 71 to 77 for nickel. The preferred metal of the

5   first thermal spray layer is selected from the group consisting of nickel, chromium, iron, zinc, and their alloys. The most preferred metal of the first thermal spray layer is selected from a group consisting of nickel and nickel alloys. The preferred method of

10 applying the polymeric layer and the layer comprising a mixture of polymeric and particulate materials is by spreading. The preferred thermal spray process for both the metallic and chromium oxide layers is plasma spray deposition.

15   FRP rolls for use in the paper industry may be coated in a manner similar to that used for anilox rolls as described above, but with an alumina-based outer coating rather than chromia-based. For these applications, the alumina is not usually laser

20 engraved.

        The following examples are provided below to illustrate the invention, but are not intended to demonstrate the full scope of the invention or limit its applicability in any way. Examples 1 to 6

25 represent comparative examples outside the scope of the invention.

Example 1.

        Many attempts were made to coat several types of

30 carbon fiber and glass fiber reinforced composite materials directly with plasma sprayed chromium oxide and with plasma sprayed nickel coatings. The surfaces

were roughened to varying degrees by grit blasting and
the deposition parameters were varied, but without
success. Virtually no deposition of chromium oxide was
achieved and the coverage achieved with nickel was
5   incomplete and the carbon fibers flared even more than
after grit blasting. A few samples were coated with a
first layer of nickel about 0.25 mm thick followed by a
second layer of chromium oxide. The bond strength of
some of these nickel/chromium oxide coatings to CFRP
10   was measured using a modified American Society for
Testing and Materials tensile bond test designed for
thermal spray coatings. The maximum bond strength
achieved was 1,100 psi (7.6 MPa) when the chromium
oxide layer was 0.175 mm thick, diminishing to near
15   zero when the chromium oxide layer was 0.300 mm thick.
These values are unacceptable for service use.

Example 2.

    An attempt was made to coat a carbon fiber
20   reinforced composite with a diluted epoxy based
material prior to attempting to deposit chromium oxide
or nickel by plasma spraying. Virtually no chromium
oxide was deposited whether it was plasma sprayed while
the epoxy-based layer was still tacky or completely
25   cured.

Example 3.

    Carbon fiber reinforced composites samples were
electroplated with nickel greater than 0.5 mm thick and
30   then ground to about 0.175 to 0.200 mm thick. Nickel
coatings about 0.125 mm thick were also produced. Both
were successfully over-coated with plasma sprayed

chromium oxide. An electroplated nickel coating about
0.125 mm thick was tested; but it spalled when a plasma
sprayed chromium oxide was applied over it. While this
approach to coating CFRP appeared to be somewhat
5   successful, its reproducibility is questioned.
Furthermore, this process requires an electroplating
facility and it would be very expensive to apply to
large components.

10   Example 4.

Carbon fiber reinforced composite samples were
coated with resin-bonded hollow microspheres which were
then ground to open the hollow spheres to provide
cavities for bonding a second coating. Some of the
15   samples were then over-coated with plasma sprayed
stainless steel. An attempt was then made to coat
these samples with plasma sprayed chromium oxide. The
underlying resin bonded microsphere coating spalled in
all cases.
20

Example 5.

Carbon fiber reinforced composite samples were
obtained that had a white gel (resin) overcoat. These
samples could be coated with a plasma sprayed chromium
25   oxide, but it was found that the chromium oxide coating
had many pinholes and small areas with no chromium
oxide coating. In addition, the white gel process was
difficult to use in production because of the excessive
amount of diluent, methyl ethyl ketone that evolved
30   during spraying resulting in: 1) creating a potential
health and fire hazard; 2) difficulty in obtaining a

uniform coating; and 3) difficulty in maintaining its uniformity while the coating was cured.

Example 6.

5   A series of experimental CFRP samples and prototype rolls were coated with the following procedure. Process parameters were optimized for each step in the procedure.

10   a) The CFRP was cleaned and then roughened by grit blasting with 60 mesh aluminum oxide grit at 20 psi and a 152 mm standoff to a surface roughness of greater than 0.003048 mm (120 microinches) Ra. The surface was then wiped with methanol or acetone.

15

    b) A mixture of an epoxy and either aluminum or nickel was produced. The epoxy was a mixture of bisphenol F/epichlorohydrin (Shell Epon 862) + 12.18 weight percent diethylenetriamine (Shell Epi-Cure
20   3223). In the case of aluminum, the mixture was 60 to 62 weight percent aluminum. In the case of nickel, the mixture was 73 to 75 weight percent nickel. The metal powders were nominally less than 44 microns in size. The viscosity changes significantly within the
25   composition ranges given, and the specific ratio used was chosen for ease of application on a specific sample or component. Great care was taken to avoid introducing air into the mixture while blending the epoxy with the metal powder. A number of attempts were
30   made to spread the mixture on the sample or component using techniques described above. None of these attempts were successful.

Example 7.

It was surprisingly found that the addition of a
thin layer of polymeric material on the FRP surface
served to enhance the bond strength and the reliability
of the coatings. The following illustrates the coating
materials and processes used to successfully coat both
laboratory samples and production prototype anilox
rolls made of carbon fiber reinforced composite
materials.

a) The CFRP was cleaned and then roughened by
grit blasting with 60 mesh (-423 µm screen size)
aluminum oxide grit at 20 psi (138 kPa) and a 152 mm
standoff to a surface roughness of greater than
0.003048 mm (120 microinches) Ra. The surface was then
wiped with methanol or acetone.

b) A thin layer of epoxy was then applied to a
thickness of 0.005 to 0.025 mm. The epoxy was a
mixture of bisphenol F/epichlorohydrin (Shell Epon 862)
+ 12.18 weight percent diethylenetriamine (Shell Epi-
Cure 3223). The epoxy was applied smoothly to the
sample or roll surface shortly (less than 20 min.)
before the mixture of epoxy plus aluminum was applied.

c) A mixture of the same epoxy as in (b) above
and either aluminum or nickel was produced. In the
case of aluminum, the mixture was 60 to 62 weight
percent aluminum. In the case of nickel, the mixture
was 73 to 75 weight percent nickel. The metal powders
were nominally less than 44 microns in size. The
viscosity changes significantly within the composition
ranges given, and the specific ratio used was chosen
for ease of application on a specific sample or
component. Great care was taken to avoid introducing

air into the mixture while blending the epoxy with the metal powder. The mixture was spread on the sample or component using a technique described above to a thickness of about 0.500 mm.

5   d)   The epoxy and epoxy/metal mixture was allowed to cure for at least three hours and then single point machined to a thickness of about 0.300 mm.

           e)   After at least 36 hours from the time the epoxy/metal mixture was applied, the surface can be

10   roughened by grit blasting using 60 mesh (423 μm screen size) aluminum oxide grit at 20 psi (138kPa) with a 150 mm standoff to a surface roughness of about 0.00508 to 0.00635 mm (200 to 250 microinches) Ra.

           f)   Optionally, a plasma deposited nickel coating

15   was then applied to a thickness of about 0.125 mm.

           g)   A plasma deposited chromium oxide coating was applied to a thickness of about 0.300.

           h)   For a prototype anilox roll, the chromium oxide coating was ground to a smooth surface and then

20   laser engraved.

           All of the samples prepared by this procedure were very acceptable. No significant surface imperfections were observed. The bond strengths of the coating systems with and without the optional plasma sprayed

25   layer were measured using a modified recommended procedure of the American Society for Testing and Materials. A tensile bond strength of 3010 psi (20.8 MPa) was measured with the nickel layer and 3200 psi (22.1 MPa) without the nickel layer. Thus the bond

30   strength for either was more than adequate for the intended service as an anilox roll. The multi-layer

structure readily achieves the 10 MPa tensile strength required for most commercial applications.

The process readily coats cylindrical rolls constructed with fiber reinforced polymer substrates such as CRFPs. First applying the two polymeric layers to a cylindrical roll's outside cylindrical surface and then thermally spraying this surface creates the multi-layer coating that effectively covers and protects the roll's working surface. This is particularly effective for articles of manufacture such as fluid metering rolls, rolls used in the production of paper and rolls used in film processing.

The multi-layered structure provides an effective coating for fiber reinforced composite polymeric materials and components. These coatings are well bonded and have an exterior layer with high resistance to wear, corrosion or other unique properties not provided by the fiber reinforced composite materials per se. In addition, it provides an improved process for applying well bonded thermal spray coatings to fiber reinforced composite polymeric materials and in particular to carbon fiber reinforced composite materials and components.

Many possible embodiments may be made of this invention without departing from the scope thereof, it is understood therefore that all matter set forth herein is to be interpreted as illustrative and not in a limiting sense.